Due to a printing error, this letter, which originally appeared in the 11 January 1993 issue, on pages 202–204, is being republished in its entirety.

Catalytic growth of carbon microtubules with fullerene structure

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A method to grow carbon microtubules with fullerene structure (buckytubes) has been identified. The method consists of the catalytic decomposition of acetylene over iron particles at 700 °C. Carbon microtubules of up to 50 μm in length are synthesized by this method. Electron diffraction and high resolution electron microscopy studies demonstrate that the structure of these microtubules corresponds to the helical structure recently reported by S. Iijima, Nature 354, 56(1991), prepared using an arc-discharge evaporation method.

The recent discovery of experimental methods to produce C_{60}(1) and higher fullerenes[2] has generated a great deal of research in both academic and industrial laboratories. Particularly interesting was the report of Iijima(3) on the growth of carbon materials with a filamentlike structure, prepared using an arc-discharge evaporation method. Iijima used electron diffraction and high resolution electron microscopy to characterize these filaments, and found that they consist of coaxial tubes of graphitic sheets. He proposed that each individual tube is formed by rolling up the graphite sheets about the filament axis in such a way that a helical pitch is formed. These tubular versions of fullerenes, buckytubes, are of great interest because of their potential applications, including the production of vastly superior fiber carbons. In addition, one may also speculate that if these microtubules could be grown uniformly, one might use them as molecular sieves or as hosts of other chemical species, possibly enabling the design of catalysts with well-define structure.

In the present work we report the growth of carbon microtubules using catalytic methods. The formation of carbon filaments from the catalytic decomposition of carbon-containing gas over metal surfaces has been known for some time,[4–8] and has been recently studied in detail by Baker and co-workers.[9,10] However, it was not recognized that these methods could be used to growth buckytubes. Our method in this particular study consists in the catalytic decomposition of acetylene over iron particles supported on graphite. Free carbon produced from the decomposition of acetylene aggregates around the metal particles and starts to grow in a needlelike structure.

The 2.5 wt % Fe/graphite samples used in this study were prepared by impregnating graphite (Johnson Matthey Elect., 99.5%) with a 40 vol % ethanol/60 vol % water solution of iron (III) oxalate. The resulting samples were heated in a quartz reactor to 250 °C for 2 h in flowing nitrogen (150 cc/min), followed by a reduction at 350 °C in flowing 10% H_2/N_2 for 5 h to reduce Fe_2O_3 to metallic iron. The carbon microtubules were grown by treating the Fe/graphite samples at 700 °C in flowing 9% acetylene/N_2 (150 cc/min) at atmospheric pressure for several hours. The samples were mounted on carbon grids for transmission electron microscopy (TEM) examination. No collodion was used on the grid, since the powder proved to be self-supporting. Samples were examined on both JEOL 100CX and JEOL 400EX electron microscopes. Some of the images obtained were computer processed in order to enhance the contrast.

High-resolution electron micrographs of Fe/graphite samples treated at 700 °C for relatively short period of time, less than an hour, indicate the formation of graphitic carbon around some metal particles [Fig. 1(a)]. In some instances the structure of this graphitic carbon corresponds to an spiral structure [Fig. 1(b)]. Most of the spirals are associated with Fe particles although a few structures not associated with particles were observed. The spiral character of this structure is demonstrated by the Fourier transform of its image [Fig. 1(c)]. This kind of structure appears to be closely related to the Icosahedral spiral discussed by Kroto and McKay.[11] It is interesting to note that in earlier reports, carbon structures corresponding to concentric circles were reported.[12,13] However, to our knowledge, this is the first time in which a spiral structure of this kind is reported for these carbon materials.

As the acetylene decomposition reaction time is increased, carbon fibers start to grow and two main structures are observed: an amorphous fiber structure indicated by letter A in Fig. 2); tubular fibers with crystalline structure, (marked with letter B in Fig. 2) and additionally in minor proportion amorphous material as well as some graphitic structures are observed. The exact amount of each type of material will depend on the heating temperature and annealing time. In the conditions of the Fig. 2 up to 65% of the carbon material formed corresponds to crystalline tubular fibers. In the latter structure the twist folding indicated by Iijima[3] is clearly seen. High resolution images of the crystalline tubes (Fig. 3) indicate that they correspond to the buckytubes reported by Iijima.[3] We have performed electron diffraction experiments similar to the ones described in Ref. 3 that confirm that these tubes have a spiral structure. An example of a crystalline tube and its corresponding selected area diffraction pattern is shown in Figs. 4(a) and 4(b). The diffraction patterns can be indexed using {*h*01} and {*hk*0} spots for hexagonal symme-

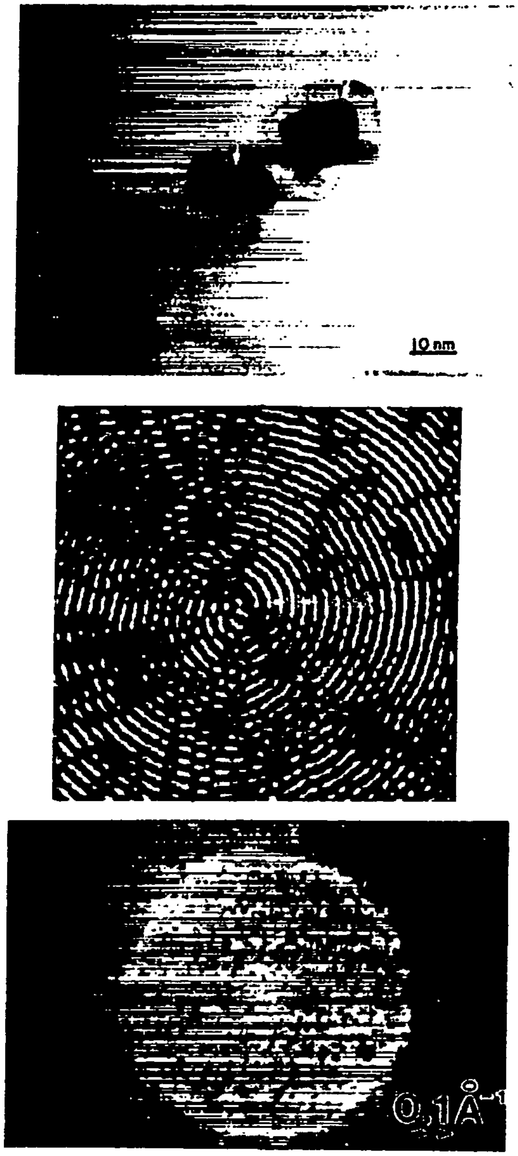

FIG. 1. (a) Formation of graphitic structures around metallic particles (arrow) which where formed by heating at 700 °C during 1 h. (b) Spiral structure formed in some regions of the same sample (a). (c) Fourier transform of the previous spiral image.

FIG. 2. Larger fiber structures formed in a long heating period (5 h) at 700 °C. Two types of structure are seen. An amorphous fiber (marked with A) and a folded crystalline fiber (marked with B).

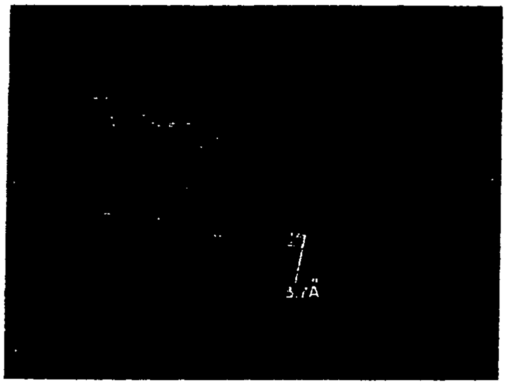

FIG. 3. High resolution image of a tube with characteristics similar to the ones described by Iijima. The distance between planes corresponds to (00.2) planes of graphite.

try. The fact that the patterns show strong (001) spots when the needle axis is perpendicular to the [001] supports the idea of a coaxial arrangement of graphitic tubes. In addition the $\{hk0\}$ patterns show mm^2 mirror symmetry about the tube axis supporting the idea of a helix around the axis. This is consisting of a helical arrangement of

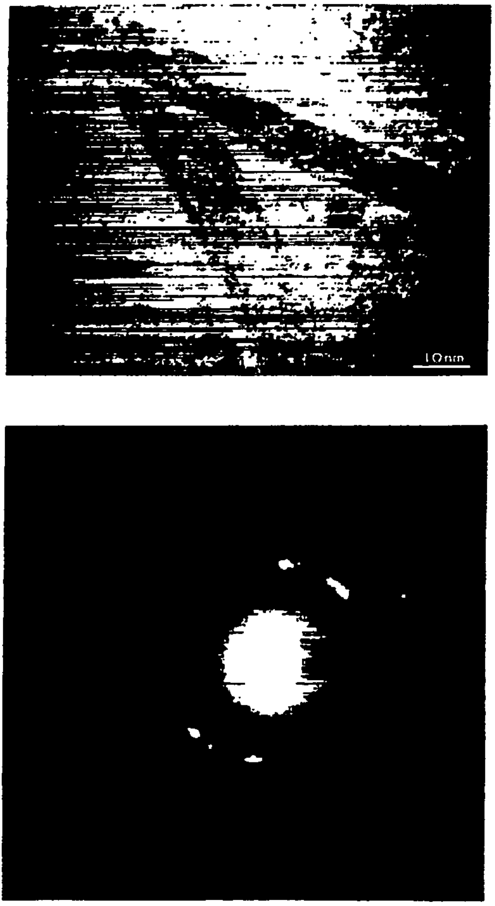

FIG. 4. (a). Image of a tubular fiber with crystalline structure and (b) its corresponding selected area diffraction pattern showing a pattern which is consistent with a spiral structure.

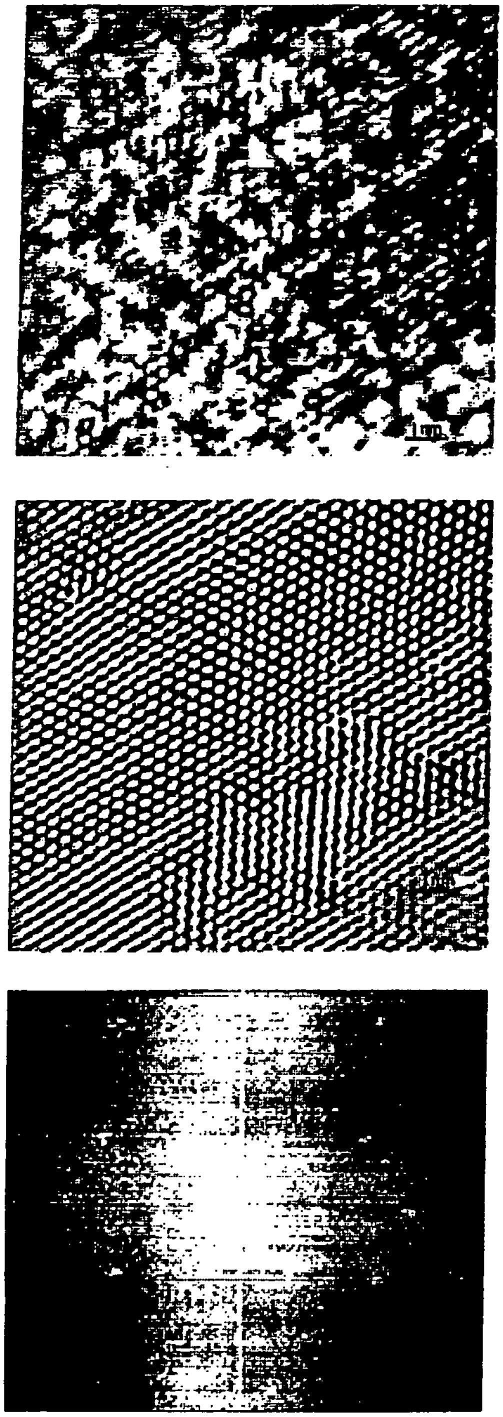

FIG. 5. Image processing of a high resolution TEM image of an amorphous looking fiber. (a) Original image, (b) crystalline portion of the image, and (c) the Fourier transform.

hexagons around the axis. Therefore we are dealing with the fullerene tubes or buckytubes found by Iijima.[3]

The amorphous looking fibers are however partially crystalline. This is clearly shown by image processing of the high resolution images. Figure 5(a) shows a high resolution image of this kind of fiber, this image can be deconvoluted. Image 5(b) shows the crystalline graphitic portion of the image. Although it is extremely difficult to make any quantitative statement about the degree of crystallinity it is clear that the fibers are not totally amorphous and have a basic graphitic structure.

We noted that the amorphous fibers have an underlying graphitic structure that can be made apparent by image processing. Therefore, these fibers are a mix of graphitic and disordered structures.

The catalytic method of growing the tubular version of fullerenes, buckytubes, allows us to produce tubes of up to 50 μm in length, and typically ranging about 50–200 Å in diameter, although tubes with diameters up to 500 Å are often observed. The diameter of the tubes is controlled by that of the metal particle from which it starts growing. The length of the tubes depends on the reaction time, as long as the metal particle was not completely covered by a carbon deposit. Iijima's method, arc-discharge evaporation of carbon, produced tubes with similar diameters to ours, but much shorter in length, only up to 1 μm.

We conclude that the catalytic method can produce tubes with fullerene structure with similar characteristics to that of the carbon-arc method described by Iijima.[3] However we distinguish two types of fibers the ones amorphouslike, and the ones with a pure buckytube structure. We however, note that the amorphous fibers have an underlying graphitic structure which can be made apparent by image processing. Therefore, this kind of tubes is a mixing of graphitic type and a disorder structure. The present method of catalytic decomposition of carbon-containing gases over metal particle presents a number of advantages, such as better control of the dimensions of the microtubules, and the possibility of producing macroscopic size fibers.

[1] W. Krätschmer, L. D. Lamb, K. Fostiroupoulos, and D. A. Hoffmann, Nature 347, 354 (1990).

[2] F. Diederich, R. Ettl, Y. Rubin, R. Whetten, R. Beak, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, C. Khemani, and A. Koch, Science 252, 548 (1991).

[3] S. Iijima, Nature 354, 56 (1991).

[4] P. L. Jr. Walker, J. F. Rakszawski, and G. R. Imperial, J. Phys. Chem. 63, 133 (1959).

[5] W. R. Ruston, M. Waezee, J. Hennaut, and J. Waty, Carbon 7, 47 (1969).

[6] S. D. Robertson, Carbon 8, 365 (1970).

[7] T. Baird, J. R. Fryer, and B. Grant, Nature 233, 329 (1971).

[8] M. Endo, A. Kathon, T. Sugiura, M. Shiralshi, Proceedings 18th Biennial Conference Carbon, Worcester Polytechnic, Worcester, Massachusetts, 1987 (unpublished), p. 151.

[9] R. T. K. Baker, Carbon 27, 315 (1989).

[10] M. S. Kim, N. M. Rodríguez, and R. T. K. Baker, J. Catal. 131, 60 (1991).

[11] H. W. Kroto and K. McKay, Nature 331, 328 (1988).

[12] R. D. Heydenreich, W. M. Hess, and L. L. Ban, J. Appl. Cryst. 1, 1 (1968).

[13] H. Kroto, Science 25, 1139 (1988).